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#### DELAYED EXCHANGE OF HYDROGEN IN SOLUTIONS OF AMMONIUM SALTS

A. I. Brodskiy, Corr Mem, Acad Sci USSR and L. V. Sulima (Inst Phys Chem in L. V. Pisarzhevskiy, Acad Sci Ukrainian SSR) Submitted 8 July 1950

According to a general mechanism of hydrogen isotope exchange in solutions which has been suggested earlier (1), one may expect that the H-D exchange between ammonium ions and heavy water proceeds very slowly. This peculiarity distinguishes ammonium ions from ammonia and amines, where the exchange at the N-H bond proceeds for all practical purposes instantaneously, and is due to the absence at the NH<sub>L</sub> ion of free electron pairs to which deuterium could add without expenditure of a considerable amount of activation energy. The same peculiarity of the electronic structure is the reason for the impeded exchange at C-H bonds and the total absence of exchange at Si-H bonds of some silanes [2]. By analogy with ammonia, it was held hitherto that exchange in ammonium ions takes place with infinite speed.

In accordance with the concept developed above, the direct exchange of hydrogen between NII, and water is either totally absent, or proceeds very slowly. The actually observed facility of exchange in ammonium salts is explained by hydrolysis and consequent formation of free ammonia. The rapid exchange takes place with free ammonia, and the latter, as a result of the reverse reaction, introduces deuterium into ammonium ions which had been originally hydrolized. At the point of hydrolysis equilibrium the concentration of ammonic is high enough to enable exchange to proceed freely in this manner, although with a measurable speed. Whenever a high concentration of a strong free acid is present, hydrolymis is

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sm pressed. Consequently, the exchange must be considerably impeded. In order to check this theory, we investigated the rate of exchange of ammonium nitrate, ammonium sulfate, and ammonium chloride with heavy water in the presence as well as the absence of the corresponding acids. The experiments were carried out in the following manner. To a weighed-in quantity of the salt dissolved in water or dilute acid a whighed-in quantity of heavy water having a known douterium content (25% D20) was added. Both liquids had been cooled to the temperature of the experiment. After a set period of time, a portion of salt for analysis of the isotope composition was separated from the solution. We encountered the difficulty that no suitable reaction for the precipitation of the ammonium ion from acidic solutions is known in the course of which the mixture is not diluted In the majority of experiments, by a considerable quantity of ordinary hydroge: precipitation was carried out by adding an excess of acetone which was dry and had been cooled to the necessary temperature. Control experiments established the complete absence of exchange with acetone under the conditions of our experiments. All operations necessary for the separation of the salt sample by this method took 1/2 to 1 minute.

In several experiments with ammonium nitrate, precipitation of the salt was effected by fracting it out. In view of the fact that this process takes 15 was effected by fraction is suitable only for a qualitative determ confirmation min, the method in question is suitable only for a qualitative determ confirmation of the fact that delayed exchange takes place. Finally, several experiments with precipitation by diomane were carried out. This procedure also required several minutes.

The precipitated salt after sucking off was dried in vacuum at 80°. The content of deuterlum in it was determined by reverse exchange of a weighed-in quantity of the dried ralt with a weighed sample of ordinary water. After completion of the exchange, a part of the water was distilled off and its density measured according to the temperature at which the hydrometer floated.

measured according to the temperature at which the state of several typical experiments on the In tables 1 and 2, the results of several typical experiments on the exchange of in ammonium nitrate and ammonium sulfate are cited. These data are not quantitative, because the precipitation took place during some period of time which was not exactly reproducible. During this time, the exchange continued under was not exactly reproducible. During this time, the exchange continued under conditions of concentrations and of a temperature which were variable.

This refers particularly to experiments in which precipitation with acetone was carried out immediately after addition of heavy water and energetic stirring. In these experiments a time of exchange equal to 1 min was arbitrarily assumed. Apparently these sources of error explain a certain quantitative inconsistency—in—the—sellatien—of—data— that becomes noticeable after the data have sistency—in—the—sellatien—of—data— that in accordance with theoretical been collated. Both tables show, however, that in accordance with theoretical concepts, exchange in the case of the ammonium ion does not proceed instantaneously, concepts, exchange in the case of the ammonium ion does not proceed instantaneously, concepts, exchange in the case of the ammonium in the presence of an excess of free acid that suppresses hydrolysis. The reduction of the rate of exchange is smeller for ammonium sulfate, because the comparatively low solubility of this salt did not permit the use of highly concentrated solutions of sulfuric acid. The solubility of ammonium chloride is still lower, and for that reason acid. The solubility of ammonium chloride is still lower, and for that reason acid. The solubility of ammonium chloride is still lower, and for that reason acid. The solubility of ammonium chloride is still lower, and for that reason solutions of 0.2 g of salt in 1 g of water at 0° gave 70-80% of exchange in 1 min, while solutions of 0.1 g of salt in 1 g of light HCl gave 55-70% of exchange under the same conditions.

The following proximate equation describes the kinetics of exchange proceeding over free ammonia in a system which is in a state of equilibrium with respect to hydrolysis:

 $-\ell_{N}\left(1-\alpha\right)=2kW\left(1+\frac{N}{W+B}\right)t$ 

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In this equation, & is the fraction of exchange with respect to equilibrium, & the rate constant of the straight line for the reaction of the hydrolysis of NH, and W, N, and B concentrations of water, salt, and the added acid respectively. In deriving this equation, we neglected the presence of molecules in which more than one atom of hydrogen is replaced by deuterium, and also the effect of isotopic exchange on the degree of hydrolysis.

While the limits of reproducibility of our data do not permit a quantitative check of this equation, it does without any doubt describe correctly the kinetics of exchange. In particular, this equation explains why in strongly acidic solutions where the concentration of ammonia is reduced by a factor of 10° with respect to the neutral solution, the rate of exchange is reduced by approximately one concentration of ammonia is reduced by approximately one concentration of ammonia.

The results of this investigation give added confirmation to the above-mentioned theory of hydrogen exchange in solution, and to the fundamental deduction
from this theory that capacity for exchange is determined by the atructure of the
electronic shell surrounding the atom rather than the nature of the bond X-H.

#### Bibliography.

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Table 1. Exchange in NH, NO3. Acid: 54% HNO3

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temperature   C°	time in min	without acid		with acid		
		g sal.t g water	% of exchange of the state of t	ge g salt g wa <b>ter</b> g acid	% of exchange	
-lo o 0 20 0 0	1 10 15 15* 2* 35**	1.14 1.04 1.11	76 82 102	0.36 0.38 0.35 0.41 0.37 0.25	23 36 58 59 64 90	

\* Precipitation by freezing out; 1/3% acid. Precipitation continued for 15 min at -10°.

Precipitation with dioxane added after expiration of the time indicated in the table. Precipitation continued for 5 min at plus 10 to plus 12°.

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Table 2. Exchange in  $(NH_{l_1})_2SO_{l_1}$ . Acid: 13%  $H_2SO_{l_1}$ 

temperature	time in min	without ac	sid g of exchang	with acid g salt g weeks	% of exchange
0 0 0	1. 5 10	0.36	95 99	0.148 0.53 0.1:1	85 90 102

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